

The Synthesis and Spectroscopic Properties of Chalcone-derived Dyes Prepared by the Aldol Condensation of 4-Acetyl-4'-dimethylamino-azobenzene and Benzaldehydes

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ABSTRACT. Aldol condensation of 4-Acetyl-[4-dimethylamino and phenylamino] azobenzene with various aromatic aldehydes gave the corresponding chalcone-derived azo dyes. The new dyes showed a broad absorptions in the visible region with medium intensities. The halochromism of these new dyes were investigated and found in accordance with the resonance theory.

Introduction

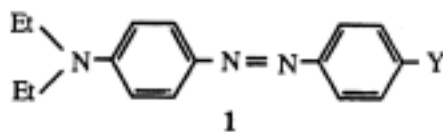
Azo dyes are the most important class of commercial dyes, importance of azo dyes due to their economy, versatility, relative ease of manufacture and good tinctorial power^[1]. The azo dyes **1a-c** derived from 4-aminobenzaldehyde have been reported^[2]. The presence of free aldehyde in dye **1a** was investigated to produce dyes absorbing at longer wavelengths. Dyes **1c** and **1b** in ethanol are blue ($\lambda_{\text{max}} = 587 \text{ nm}$) and violet ($\lambda_{\text{max}} = 523 \text{ nm}$) respectively. In the present paper, the use of 4-amino acetophenone as diazo component was undertaken, and for comparison purpose two coupling components were used, namely N,N-dimethylaminoaniline and diphenylamine. The resultant dyes **2b** and **3b**, were found to undergo an aldol condensation with various aromatic aldehydes to give novel chalcones **2c-f**, **3c-d** and **3f-g**.

Results and Discussion

Synthesis of dyes

4-Aminoacetophenone was diazotised smoothly in an aqueous mixture of hydrochloric and acetic acids at 0-5°C on addition of sodium nitrite as described

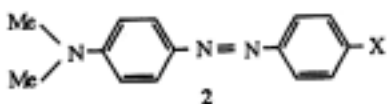
by Hodgson and Beard^[3]. The diazonium ion could be coupled in good yields to the coupling components in aqueous hydrochloric acid at 0-5°C, with addition of sodium acetate. Dyes **2b** and **3b** were obtained in 93 and 95% yield respectively. The dyes showed absorption maxima in ethanol at 443 nm for **2b** and 451 nm for **3b**. The presence of the free acetyl group was indicated by an intense $\nu\text{C}=\text{O}$ peak in the IR spectra at 1674 cm^{-1} for **2b** and at 1668 cm^{-1} for **3b**.



a : Y = CHO

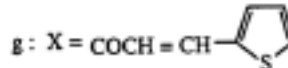
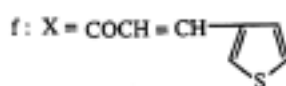
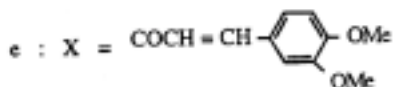
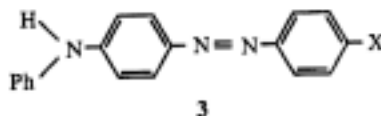
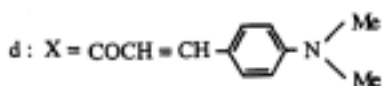
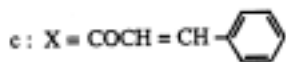
b : Y = CH = C(CN)₂

c : Y = C(CN) = C(CN)₂



a : X = H

b : X = COCH₃



The acetyl groups of dyes **2b** and **3b** were found to undergo an Aldol condensation^[4] with aromatic aldehydes giving the novel dyes **2c-f** and **3c-d, 3f-g**. The ir spectra of dyes **2c-f** showed absorption for C = O in the region of $1640-1674\text{ cm}^{-1}$ and in the region of $1649-1668\text{ cm}^{-1}$ for dyes **3c-d** and **3f-g** indicating of the conjugation (Table 1). The dyes were characterised by micro-analysis and FT-IR spectra. Yields, melting points, colour of crystals and micro-analytical data are summarised in Table 1.

TABLE 1. Physical, analytical and IR data of synthesised dyes.

Dye no.	Yield (%)	M.P (°C)	Colour of crystals	Formula	Found (calc.) %			V _{max} (cm ⁻¹)	
					C	H	N	v(C=O)	v(C=C)
2b	93	160	Dark-red	C ₁₆ H ₁₇ N ₃ O	71.82 (71.91)	6.15 (6.36)	15.60 (15.73)	1674	1605
2c	93	130-132	Orange	C ₂₃ H ₂₁ N ₃ O	77.50 (77.70)	5.80 (5.99)	12.10 (12.00)	1672	1601
2d	94	185-187	Orange-red	C ₂₅ H ₂₆ N ₄ O	75.01 (75.30)	6.35 (6.53)	13.79 (13.98)	1644	1597
2e	92	155	Orange	C ₂₅ H ₂₅ N ₃ O ₃	72.11 (72.30)	6.15 (6.02)	10.34 (10.12)	1640	1600
2f	95	155-157	Red	C ₂₁ H ₁₉ N ₃ SO	70.01 (69.81)	5.09 (5.29)	11.50 (11.64)	1661	1605
3b	95	154	Red	C ₂₀ H ₁₇ N ₃ O	76.39 (76.19)	5.51 (5.39)	12.99 (13.30)	1668	1590
3c	96	150-151	Brown	C ₂₇ H ₂₁ N ₃ O	80.21 (80.39)	5.11 (5.21)	10.22 (10.42)	1649	1603
3d	89	165	Brown	C ₂₉ H ₂₆ N ₄ O	78.25 (78.03)	5.55 (5.83)	12.40 (12.56)	1657	1593
3f	90	160	Red	C ₂₅ H ₁₉ N ₂ SO	75.80 (75.95)	4.71 (4.81)	6.91 (7.10)	1658	1590
3g	92	142	Brown	C ₂₅ H ₁₉ N ₃ SO	73.31 (73.20)	4.53 (4.89)	9.91 (10.19)	1655	1599
5	95	85	Deep yellow	C ₁₇ H ₁₈ N ₂ O	76.75 (76.90)	6.52 (6.77)	10.41 (10.52)	1661	1604

Visible absorption spectroscopic properties

Visible absorption spectroscopic data for dyes series **2** and **3** are summarised in Table 2. The parent dye **2a** showed λ_{\max} at 407 nm in ethanol^[5], which may be compared with the absorption maximum for **2b** at 443 nm in the same solvent. Thus, the introduction of acetyl group in the diazo component exerts a significant bathochromic shift of ca. 36 nm due to shift of the electron density from donor part of chromophore to acceptor and on absorption of light. Comparison of dyes **2a** and **3a** showed that the diphenylamine system is slightly more bathochromic than the dimethylaniline system.

TABLE 2. Halochromism of synthesised dyes 2 and 3 in CH₂Cl₂.

Dye no.	λ_{\max} (ethanol)	Neutral			+ HCl			$\Delta\lambda_c$
		λ_{\max} (nm)	ϵ_{\max}^a	$\Delta v_{1/2}^b$	λ_{\max} (nm)	ϵ_{\max}^a	$\Delta v_{1/2}^b$	
2b	443	359	14.0	71.4	558	14.0	74.6	+ 199
2c	444	454	18.5	75.8	548	18.6	80.6	+ 94
2d^d	445	425	13.6	102.0	516	15.5	111.0	+ 91
2e	443	464	21.0	71.4	528	22.0	86.2	+ 64
2f	450	459	18.8	73.5	562	18.9	75.8	+ 103
3b	451	421	16.4	82.0	522	16.5	61.8	+ 101
3c	456	431	20.8	83.3	544	21.1	57.4	+ 113
3d	449	429	14.7	110.0	527	66.8	109.0	+ 98
3f	457	436	20.5	86.2	535	30.4	102.0	+ 99
3g	451	439	17.1	79.4	524	21.5	70.0	+ 85

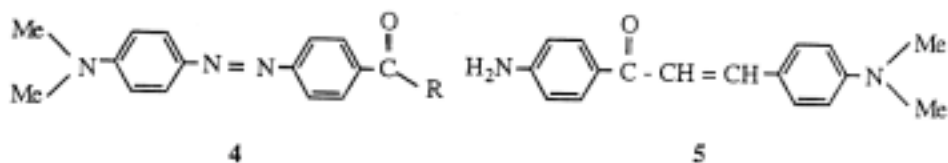
a $L \text{ mol}^{-1} \text{ cm}^{-1} \times 10^{-3}$

c $\Delta\lambda = \lambda_{\max}(\text{azonium}) - \lambda_{\max}(\text{neutral dye})$

b Band width at half absorbance $\text{cm}^{-1} \times 10^{-3}$

d in ethanol

Dyes **2d** and **3d** can be considered as a combination of the two independent chromophors described by formula **4** and **5**.

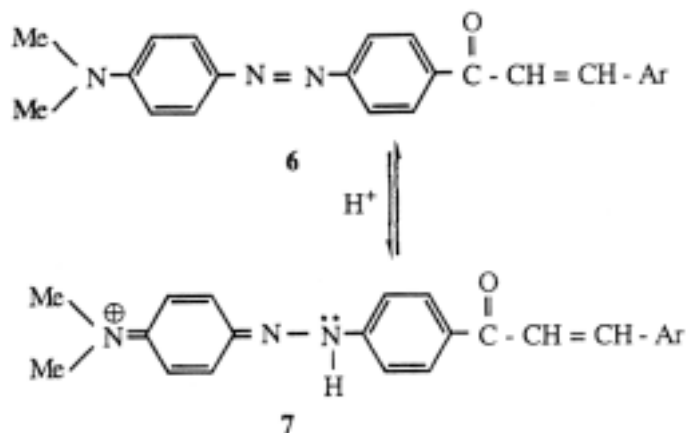


Dye **4** (R = H) showed λ_{\max} at 448 nm^[6], compared to chalcone **5** which showed λ_{\max} at 412 nm both in ethanol. The dye resulted from the combination of these two chromophors **4** and **5** is dye **2d**, which exhibited λ_{\max} at 443 nm in ethanol.

In the synthesised dye series **2** it's possible to assess the relative effectiveness of the various chalcone-derived residues ($\text{COCH} = \text{CH-Ar}$) in producing a bathochromic shift, and the sequence for λ_{max} values $2\text{e} > 2\text{f} > 2\text{c} > 2\text{d}$ is observed in dichloromethane (Table 2). Thus the chalcone-derived from *N,N*-dimethylaminobenzaldehyde is the most effective and the chalcone-derived from benzaldehyde is the least effective in producing a red shift.

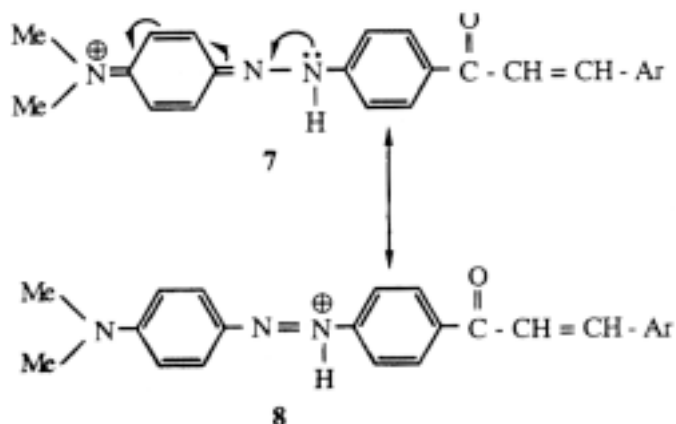
Halochromism effects

It is common for aminoazo dyes to show marked colour changes in solution in the presence of acids. Dyes **2** and **3** showed positive halochromism (*e.g.* bathochromic shift) in dichloromethane on addition of one drop of hydrochloric acid (Table 2). Halochromism in the aminoazo dyes is due to protonation of the azo group, at the nitrogen atom more remote from the amino group^[7]. It is well known that the red shift increases as the electron-withdrawing nature of the acceptor ring decreases^[8].



SCHEME 1

It is worth noticing that, the parent dye **2a** showed the most positive halochromism in the dye series **2** (Scheme 1). The introduction of the chalcone moiety ($\text{COCH} = \text{CHAR}$) decreases dramatically the positive halochromism by more than half (Table 2). This decrease can be explained based on the fact that, the electrons flow in the neutral dye from the dialkylamino nitrogen towards azo group due to component aromatic system on absorption of light. However, in the protonated species **7** the electrons migrate from the protonated azo nitrogen atom towards the dialkyl amino group *e.g.* **8** (scheme 2), thus any electron-withdrawing group in the phenyl group connected to that nitrogen atom will show a hypsochromic effect.



SCHEME 2

The bandwidths of the protonated species of dyes **2b-f** are larger than that of the neutral species, which in good agreement with reported theoretical study of some azo dyes^[9].

Experimental

Diazotisation of 4-aminoacetophenone

4-Aminoacetophenone (10 g, 0.074 mol) was dissolved in a (3:1) mixture of acetic and sulphuric acids with stirring at room temperature for 5 minutes and cooled to 5°C. Sodium nitrite (5.1 g, 0.074 mol) was dissolved in water (25 ml) and added in one portion with stirring at 5°C. The mixture was maintained at 5°C for 15 minutes, and small amount of urea was added to destroy the excess nitrous acid. The solution was diluted with ice-water (220 ml).

General procedure for coupling diazotised 4-aminoacetophenone to N,N-dimethylaniline and diphenylamine

The arylamine (0.07 mol) was dissolved in a mixture of concentrated sulphuric acid (5 ml) and ice-water (150 ml). To this mixture was added sodium acetate to give a pH of ca. 4, and the diazonium solution was added dropwise with stirring at 5°C. The stirring was continued for 3 hours. The resulting dyes **2b** and **3b** were then filtered off, washed with water until the washings were neutral, and finally washing with aqueous ethanol, and dried.

General procedure for Aldol condensation of azo dyes 2b and 3b with aromatic aldehydes

The azo dyes **2b** or **3b** (2 mmol) and the aromatic aldehyde (2 mmol) were dissolved in warm absolute ethanol (50 ml). Sodium hydroxide solution (10% w/v) in ethanol-water (20 ml) was added dropwise with stirring at 35°C, the stirring was continued overnight at room temperature. Water (100 ml) was added, the resultant dye was then filtered and dried. The crude produce was recrystallised from ethanol and characterised by microanalysis and IR spectral data (Table 1).

Synthesis of 4'-dimethylamino 4-aminochalcone 5

This was obtained using p-aminoacetophenone and p-dimethylaminobenzaldehyde using the same procedure for synthesis of chalcones in section 3.3. Characterizations are given in (Table 1).

Conclusions

New chalcones-derived dyes containing 4-dimethylamino 4-phenylamino azobenzene are prepared and their electronic properties have been investigated. The dyes showed a positive halochromism in accordance with resonance theory.

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التحضير والخواص الضوئية لأصبغ مشتقة من الشالكون
عن طريق تكاثف ألدول لمركب ٤-أسيتيل-٤-ثنائي ميثيل
أمينو آزوبنزين والألدهيدات

عبد الله محمد عسيري

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جدة - المملكة العربية السعودية

المستخلص . تم إجراء تكاثف ألدول لمركب ٤-أسيتيل-٤-ثنائي أمينو وفينيل أمينو) آزوبنزين مع الألدهيدات العطرية فأعطى مشتقات الشالكونات لأصبغ الأزو المقابلة . أظهرت الأصبغ الجديدة حزم امتصاص في المجال المرئي بشدة امتصاص متوسطة . وقد تم بحث أثر إضافة الحمض ووجد متمشياً مع نظرية الرنين .